

Memristive sensors for pH measure in dry conditions



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ABSTRACT

A large progress in pH sensing with nanowire based ion-sensitive field-effect transistors (ISFETs) has been demonstrated over the years. The electrochemical reactions occurring at the wire surface-to-electrolyte interface play a key role in the detection of ions. In this letter, we show that pH sensing can also be performed on dried samples, through electrical measurements in air with a new kind of memristive sensor. The detection of different concentrations of $[H^+]$ is confirmed by both the increased conductance and hysteretic voltage gap of the wires. The observed change in the electrical properties with pH in dry conditions is related to the formation of a wet film at the nanowire surface. Ions from the initial solution are free to move in the final water thin film at the sensing interface with consequent polarization of the NW surface.

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1. Introduction

In recent years, *silicon nanowires* (SiNWs) have attracted considerable interest due to their potential use as sensing units in integrable bio- and chemical sensors [1,2]. In particular, *silicon nanowire field-effect transistors* (SiNW-FETs) have been largely studied for detecting species in liquid solutions; the model case is represented by pH sensing [3]. Thanks to their high sensitivity and the vast knowledge of the chemical modification of the silicon oxide surfaces with active groups [4,5], they can be indeed used as high performance *ion-sensitive field-effect transistors* (ISFETs).

In the ISFET technology, the gate insulator (commonly silicon dioxide (SiO_2)) is exposed to an ionic solution, which modulates the threshold voltage, V_T , of the transistor, as a pure result of the surface interaction of the insulating material with the ions in the electrolyte. This interaction reveals itself as a change in the conductivity of the underlying channel and hence in the current flowing through it [6–8]. In the case of SiNW-FETs, the gate insulator is replaced by the native or deposited oxide that is covering the silicon surface of the nanowire. According to the site-dissociation model [9–11], charging of the surface and conductivity variation result from the ability of the amphoteric surface sites of inorganic oxides (hydroxyl groups) either to release and/or bind hydrogen ions to and from the solution in a dynamic exchange process. Their protonation state changes with the pH of the surrounding analyte.

So far, nanowires have been proposed several times as ISFET for pH [3], cancer markers [12] or DNA [13] detection in fluid environment. However, these promising results have been also accompanied by related issues regarding the scarce sensitivity and reproducibility of the conductance-based approach in fluid as consequence of Debye screening effects [2]. Moreover, different electrical features, such as the memristive effect discovered in nanoscale devices [14], have never been explored and considered as actually applicable for biosensing and pH measurement. Memristors have attracted much attention in the last years, especially thanks to their very powerful properties for constructing digital [15], analog [16], and resistive switching memories [17,18], logic [19] and neuromorphic [20] circuits. A memristive system is a passive device that cannot store energy, but that remembers the total charge transfer due to the metastable changes of its conductance [21]. Several nanofabricated devices have been found to manifest memory effects similar to those described by Chua and Williams [22,23]. In these structures, the memory effects depend on charge carrier rearrangement at the nanoscale as due to external perturbations [24]. Recently, very promising results have been reported on the use of the memristive behavior of SiNWs for sensing biological molecules in dry conditions [25,26], thus opening a promising new research line. These devices have been characterized [26,27] and demonstrated to feature the main fingerprints of a memristive system, such as the dynamic current–voltage curves of a pronounced double loop shape, the pinched hysteresis-loop, and its frequency-dependence [22]. The biodetection of these memristive sensors is revealed by changes in the so called voltage-gap [26,28], that describes the modifications of the memristive effect in SiNWs when in contact with biomolecules.

In the present paper, we investigate the possibility of sensing pH variations in dried samples measured in air for high sensitivity

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measurements [29]. In particular, we believe that the detection of hydrogen ions of a salt solution deposited and dried onto the device occurs thanks to the formation of a liquid thin film on the sample surface by adsorption of water molecules from the surrounding environment to the native oxide of the nanowire. We firstly confirmed this result by referring to the ISFET theory [6] and observing the increased conductance in p-type nanowires as a function of increasing pH values. The used solutions were brought into contact with the NW surface and dried over it before the electrical measurement. Additionally, we demonstrate as first the possibility of pH detection in air with memristive sensors thanks to changes in the voltage gap [26,28].

2. Experimental

2.1. Silicon nanowire fabrication

Memristive sensors were fabricated through a top-down, CMOS-compatible technique on a *Silicon-on-Insulator* (SOI) wafer. The process flow starts with the patterning of Nickel (Ni) contacts on the Silicon device. A 120 nm thick polymeric photoresist is spin coated onto the wafer and then patterned by *Electron Beam Lithography* (EBL). A 30 nm layer of Ni is evaporated onto the substrate, and then annealed in forming gas by successive exposure of 20 min at 200 °C, 300 °C and at 400 °C, respectively. Thus, Nickel Silicide (NiSi) contacts are realized. Piranha solution is then used to remove all the excess of Ni. In order to do that, a second EBL mask is used to define the silicon nanowires. The wafer is prepared with a 50 nm thick *Hydrogen Silsesquioxane* (HSQ) layer, used as negative tone resist for EBL. The crystalline Silicon substrate is etched by a dedicated Bosch plasma etching, in which an alternated *Deep Reactive Ion Etching* (DRIE) technique leads to free-standing, vertically stacked Si nanowires anchored between two NiSi pillars [30]. NWs with a length of 411 ± 14 nm and 1000 ± 14 nm, and a diameter of 35 ± 10 nm and 90 ± 9 nm, respectively, were fabricated and used for testing. The reported values represent data averaged on 10 NWs with same nominal size; the error stands for the standard deviation of the mean.

2.2. Chemicals

Saline solutions with different pH were prepared and used for the experiments. The pH of a starting 150 mM NaCl solution was moved towards either bigger or smaller values by adding small volumes of base or acid solutes. NaOH was used as base and HCl as acid.

Chemicals, such as NaCl, NaOH and HCl, were purchased from Sigma, Switzerland.

The pH was tested by means of a pH-meter (pHEnomenal pH Lab Set pH1000L by VWR).

2.3. Electrical measurements

To understand the effect of the pH on memristive sensors in air, electrical measurements were acquired on several devices with the use of a Karl Suss PM8 Manual Probe Station and an Agilent B1500A Semiconductor Device Analyzer. Source to drain I_{ds} - V_{ds} characteristics were registered at a fixed back-gate potential V_{bg} of 0 V. I_{ds} - V_{ds} curves were acquired in the linear scale by sweeping the source-to-drain potential from 0 to 5 V. This data was used to study the varying conductance [31], calculated as the slope of the curve, with varying pH. Current to voltage characteristics were also acquired in the logarithmic scale while double sweeping V_{ds} was between -5 and $+5$ V. These second measurements enabled us to observe the changing hysteresis properties of the memristive sensors as a function of the ion concentration. The hysteresis is studied in terms of voltage gap calculated between the forward and backward current minima of the I_{ds} - V_{ds} curves [26].

All measurements were performed on dried samples. The memristive sensors were incubated for 1 h, at room temperature, in a saline solution,

by depositing a drop of NaCl onto the devices. The solution was prepared as described in Section 2.2 and its pH was checked with a pH-meter just before use. After exposure to the fluid, the devices were gently dried under a N_2 flow, and then loaded inside a measurement chamber where they were left for about 15 min in order to get steady equilibrium condition. I-V characteristics were thus acquired from one device at one time as described here above. The electrical tests were performed at room temperature, and the humidity of the chamber was controlled and kept constant at 47% during the acquisition [28].

3. Results and discussion

3.1. SEM imaging

Fig. 1 shows the *Scanning Electron Microscope* (SEM) image of a fabricated memristive device. As a consequence of the limited and challenging sizes of the wire, the surfaces of the realized structures are not yet flat and smooth as desired. Nevertheless, by means of a top-down fabrication process, compatible with the well known CMOS technology, we managed to form NWs with the very small diameter of 35 ± 10 nm. Fig. 1a reports one of the fabricated wires, the smallest in diameter among the ones we tested. With this result we made sure to work in the high sensitivity regime of nanowire based sensors. Indeed, as already experimentally demonstrated, the width of the wire is an important factor for high performance sensing measurements [32]. A side view of the same device shows the fabricated vertically stacked nanowires anchored between two NiSi pillars (Fig. 1b).

3.2. pH sensing in air

Fig. 2 illustrates the I_{ds} - V_{ds} characteristics acquired on a vertically stacked SiNW of length 411 ± 14 nm and width 35 ± 10 nm. The source to drain curves were measured in air according to the measurement protocol described in Section 2.3. The solid line refers to a solution at pH 3.2, the dashed line to one at pH 6.2, and the dotted line to one at pH 12.3.

The figure shows an evident shift of the current towards higher values as a function of the pH; this is confirmed by the increased slope of the curve registered in less acid solutions.

The reported result is in agreement with data in literature concerning the pH sensing with the ISFET in liquid [2]. The enhanced conductance measured for increasing pH values demonstrates the sensing of decreasing concentration of hydrogen ions in the electrolyte. This result confirms the gating effect of negative charges on nanowires. The increase in conductance with increasing pH is indeed consistent with a decrease of the surface positive charges, which “turns on” the p-type SiNW via the accumulation of carriers [33,3].

Since we registered the sensitivity of memristive SiNWs to different pH, with results comparable to the ones registered in solution with the ISFET technology, we can deduce that a liquid-like thin film has to be formed at the wire surface [34] in order to let the interface phenomena reported above take place. Two main factors confirm this observation. The first one is related to the sensitivity of SiNWs to the environment humidity [28]. Nanowire and nanotube field effect transistors lying on a SiO_2 surface exposed to the ambient environment show hysteresis due to the charge trapping by water molecules existing all around [35,28,36]. Secondly, water adsorption also occurs on dried salt clusters [37] and organic layers [38], as well as on our device due to the drying of highly concentrated NaCl solution. Thus, a water film is adsorbed on the surface of the nanowire, and the deriving aqueous environment enables the dissolution of the salt, and the movement of the ions towards the hydroxyl groups of the native oxide at the nanowire surface [34].

According to the Gouy–Chapman–Stern model, the only ion species that approaches the surface of the insulator is the $[H^+]$ ions, since these ions are small enough and poorly hydrated by water molecules [39],

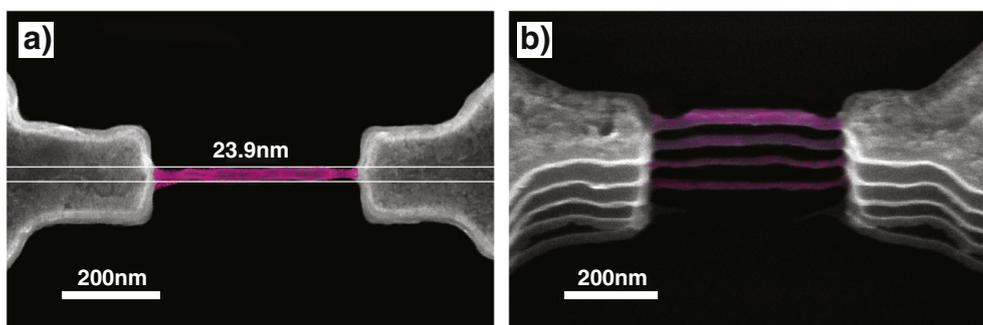


Fig. 1. SEM image of the smallest fabricated memristive sensor. (a) Top view revealing the nanoscale structure; (b) side view showing four vertically stacked SiNWs.

unlike the ions of other dissolved species (NaCl). Indeed, the augmented conductance is the result of increasing concentrations of $[\text{OH}^-]$; i.e., it only derives from the pH variations of the formed liquid film.

More important, we show here that the novel approach based on the hysteresis of memristive sensors in air is used to sense pH, too.

As already mentioned, silicon nanowires manifest a memory effect on the voltage scan across the nanowire, as indicated by the different I_{ds} values assumed by the I_{ds} - V_{ds} characteristic for same V_{ds} . This hysteresis presents the memristive character [26,28,30] due to the charge trapping occurring inside the nanowire [35,27]. An example of hysteresis “double” loop, typical of memristive devices and measured on the fabricated SiNWs, is shown in Fig. 3. In previous papers, we demonstrated that a voltage gap measured in between the forward and backward current minima appears when biomolecules are immobilized onto the nanowire surface, and its changes are used for the detection of increasing concentrations of analytes [25,26]. In the present letter, we show that the memristive voltage gap variation also works for pH measurements.

Fig. 4a reports the mean behavior of the voltage gap as function of increasing pH. In particular, each point represents the mean of the voltage gaps calculated from the hysteretic curves acquired on five SiNWs 411 ± 14 nm long and 35 ± 10 nm wide. The error bars in the graph stand for the standard deviation. The calibration line (dashed line) clearly shows the rising behavior of the voltage gap as a function of the increasing pH of the solution to which the sensor was exposed for 1 h before drying. The error in the calculation of the voltage gap calibration curve is quite relevant. The high variability can be attributed

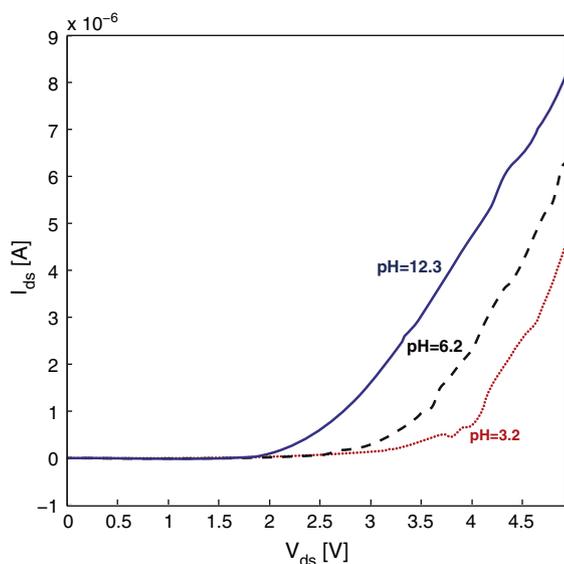


Fig. 2. Increased conductance as a function of increasing pH values. Solid line, pH 3.2; dashed line, pH 6.2; dotted line, pH 12.3.

to defects easily insertable with fabrication processes that are not fully repeatable. The SiNWs come from the same fabrication batch. However, as known from the literature, the fabrication of nanowires via top-down processing (Section 2.1) does not yet have the repeatability properties of a bottom-up method. The final structures, although similar, still show a relevant error of reproducibility, as actually showed by the standard deviation in the size calculation of the SiNW width and length, and the actual roughness of the nanowire surfaces (Fig. 1). These factors, together with a possible non-homogeneous drying of the saline solution onto the devices, and slight changes of humidity conditions occurring in the chamber, explain the big deviation of the voltage gap values. Despite this, the wires behave very similarly if taken singularly, i.e. the voltage difference between the forward and backward current minima of the memristive curve clearly show an increase as an effect of the pH of the starting solution. This effect is especially amplified for high pH values, while a still low sensitivity is demonstrated for points below the pH neutrality. A bigger population of data can reduce the error and improve the measurement accuracy.

Fig. 4b shows an example of hysteresis in the I_{ds} - V_{ds} characteristic calculated from one memristive NW of the tested set; it was measured just following the fabrication process (dashed line) and then after its exposure to the NaCl solution at pH 12 and subsequent drying (solid line). Noticeably, the nanowires are behaving as ideal memristors with pinched hysteresis loop [21] before any incubation in salt solution is performed. The memristivity of the SiNW is then modified by contacting the sensor with an electrolytic medium (dashed line). Further insight in the physical analysis of the phenomena is still required. Nevertheless, the clear modification of the hysteresis, with forming and varying voltage gaps occurring upon exposure to ionic solutions,

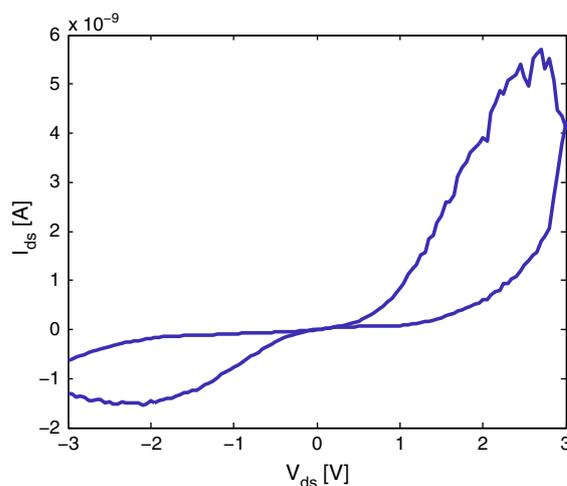


Fig. 3. Hysteresis in SiNWs. The pinched hysteresis loop is index of memristive effects in the fabricated devices.

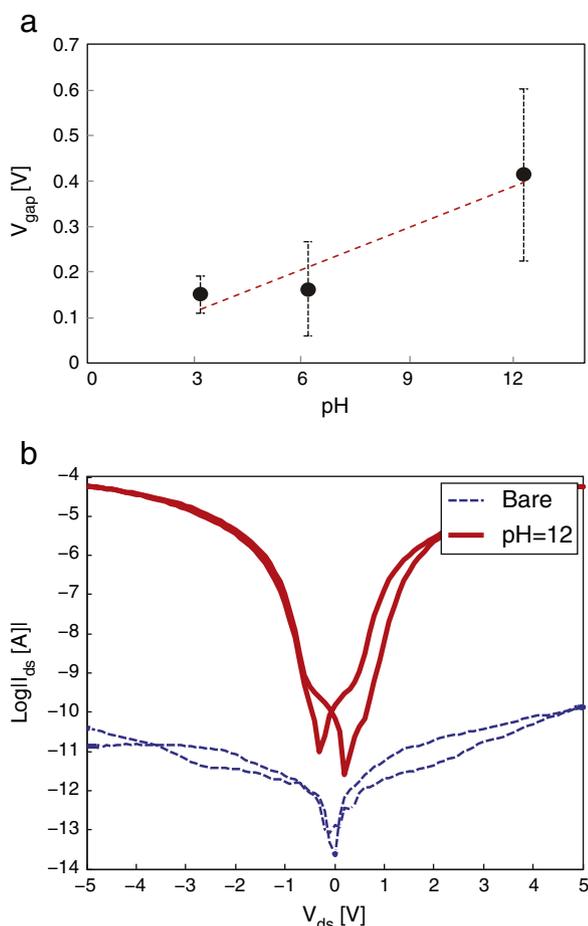


Fig. 4. (a) Increasing hysteric voltage gap as function of varying pH calculated on memristive sensors 411 ± 14 nm long and 35 ± 10 nm wide. (b) Increased voltage gap in the hysteric $I_{\text{ds}}-V_{\text{ds}}$ characteristics of the NWs before (dashed line) and after (solid line) exposing for 1 h and then drying a NaCl solution at pH 12 at the sensor surface.

demonstrates that this behavior is related to the concentrations of ions “released” from the starting solution and charging the SiNW surface. These charges happen to change the electrical properties of the memristive sensors in a predictable way. The result has been also confirmed by testing bigger NWs having a length of 1000 ± 14 nm and a diameter of 90 ± 9 nm. The dependence of the voltage gap on the pH is also in agreement with previous finding on the effect of charged biomolecules all around the memristive sensor [26,28].

In the presented approach for pH sensing, the charge effect from ions on the voltage gap variation is measured after everything has been dried; we thus believe that a liquid-like thin film is formed at the nanowire surface [34]. The hysteresis of the $I_{\text{ds}}-V_{\text{ds}}$ characteristics consistently confirmed the previously observed effect of the humidity on our NWs [28]. Accordingly, water molecule adsorption is favored by salt clusters forming after drying the sample [37]. As a consequence, an ionic liquid thin film is formed, and this allows for the detection of either the base or acid behavior of the buffer solution [34]. Variations of the concentration of positive hydrogen ions of the electrolyte affect the voltage gap. An excess of negative ions, such as $[\text{OH}^-]$ in the solution, leads to the increased voltage memory in the memristive device.

4. Conclusions

In this letter, we have shown the possibility of sensing pH variations with measurements in air performed with memristive sensors in dry conditions. The detection of a different amount of hydrogen ions of a salt solution deposited and dried over the sensor is confirmed by both

the increased conductance and the hysteric voltage gap of the wires. These results are demonstrated in nanowires with different widths and lengths. Data acquired while measuring in air are in good agreement with the literature on ISFET technology for detection in solution, and show further development in the use of the memristive effect for sensing. In addition, the conductivity behavior as a function of increasing pH, and the existence of varying hysteresis properties upon deposition and drying of an electrolyte on top of a device, reveal the formation of a liquid-like thin film at the device surface that enables the interface phenomena leading to pH sensing.

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